Preparation of Tin Single Crystals

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In the previous investigation,[1] the three types of glass mould a, b and c shown in Fig. 1 were used to produce the spherical tin single crystals by the Bridgman's method, and it was found that the type c is most effective. It is considered that the single crystals produced by using the glass mould of the type c mentioned above may be oriented to be nearly parallel to a certain crystal direction.

In this study, therefore, the orientation of the rod single crystals of tin (99.8 % in purity) produced by the same method as before, using the glass mould d shown in Fig. 1, was analyzed with X-rays.

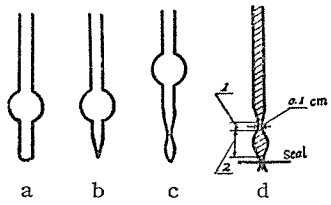

Fig. 1. Glass mould of various types.

Investigations concerning the imperfection of the tin crystals —the so-called line structure in which many parallel lines appear on the surface of crystals— were reported by B.Chalmers,[2] A. T. Goss[3] and R.B.Pond[4] : B. Chalmers explained it as the "macro-mosaic structure", and A. T. Goss ascribed it to impurities, while R. B. Pond insisted that the line structure would be observed even on the crystal of ideal purity.

In this study, the line structure was also examined by the microscope with the three kinds of tin of 99.98 (impurities-Cu, 0.00415; Pb, 0.0035; Fe, 0.00155; Bi, 0.00065; Zn, 0.0015; As, 0.0009; Sb, 0.0011) 99.8 (impurities-Pb, 0.05; Cu, 0.03; Fe, 0.02; Sb, 0.03) and 98 percent in purity.

EXPERIMENTAL METHOD

The mould of the type d shown in Fig. 1 was made from the pyrex glass tube of 3 ~ 5 mm. in innner diameter and its sizes are given in the figure. The lower end of the glass mould was pushed in the vessel holding the molten tin and after the molten tin was sucked into the glass mould, the mould was sealed as shown in the figure. The temperature distribution in the electric furnace wound with the nichrom wire, is given in Fig. 2 and the temperature gradient at 232°C (melting point of tin)

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in the furnace was about 13°C/cm. After holding the lower end of the mould containing the metal at the point A, indicated in Fig. 2 (308°C) in the furnace, it was lowered

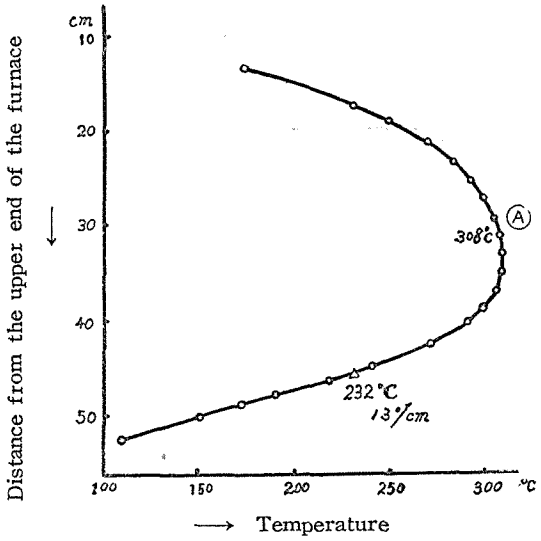

Fig. 2. Temperature distribution in the furnace at a stationary state.

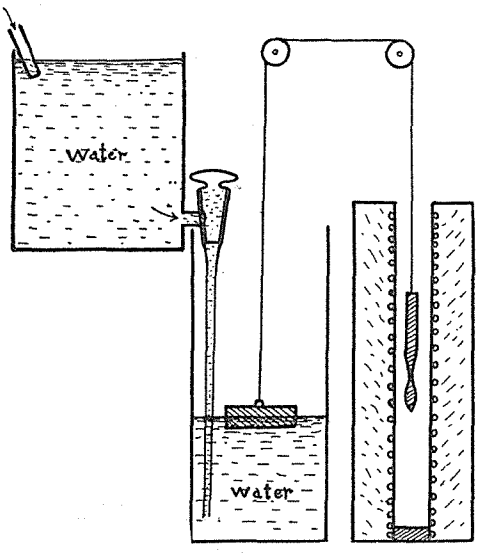

Fig. 3. Apparatus lowering a mould with tin metal.

at a constant velocity in air by the apparatus shown in Fig.3 After this operation the glass mould was sunk into the hydrofluoric acid in order to take out the tin crystal from it. In this case great care must be taken to prevent the straining or twinning of the crystal by an excessive pressure. An X-ray analysis was performed to determine the orientation of rod single crystals thus produced, by transmitting X-rays perpendicularly to the disk-shaped specimen cut off perpendicularly to the rod axis.

EXPERIMENTAL RESULTS

(1) X-Ray Analysis

Thirteen single crystals prepared under the conditions given in Table 1, were analyzed by the X-ray Laue pattern, and the stereographic projection of the directions of their rod axes with respect to the crystal axes, is given in Fig. 4. It may be seen

Table. 1. Preparing conditions.

No. of Specimens	Max. Molten Temp. °C	Cooling Velocity cm./hr.
15	308	4.5
2	〃	4.7
3	〃	4.7
18	〃	5.0
20	〃	5.5
16	〃	7.0
23	〃	7.5
24	〃	7.5
22	〃	8.0
27	〃	8.0
11	〃	9.0
12	〃	9.0
28	〃	11.0

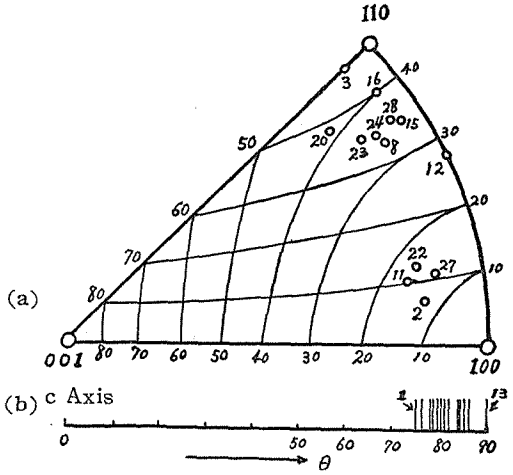

Fig. 4.

(a) Stereo-projection figure of the rod axis of each single crystal.

(b) Angles from the c-axis — the real angles of each position are given in the table shown below. In this table, the number of line is counted from left to right.

No. of lines	1	2	3	4	5	6	7	8	9	10	11	12	13
No. of specimens	22	20	11	24	2	27	23	18	16	3	28	15	12

from this figure that the angles between the c axis ([001]) and the rod axes are all in the range of 75 and 90 degrees. Whether the directions are nearer to the one among the [110] direction or the [100], can not be decided owing to the small number of observations, but it may be somewhat nearer to [110]. It seems too, that the cooling velocity has practically no effect on the inclination of the rod axis with the [001] direction, in the range of cooling velocities between 4.5 and 11.0 cm./hr., which we can control.

(2) Effect of Cooling Velocity

On the specimen of 99.8 percent in purity the cooling velocity up to 20 cm./hr. might be admitted to realize the success of 100 percent, using the type d shown in Fig. 1 to prepare the single crystals. On the other hand, in the case of the cooling velocity over 20 cm./hr., the specimen was made of two or many crystals.*

The results of specimens of 99.98 and 98 percent in purity were the same as those of 99.8 percent, with the cooling velocity up to 20 cm./hr.

(3) Imperfection of Single Crystals

It was found from the back reflection Laue pattens, that the single crystals prepared by the above method were not ideal crystals but were made of small rod crystals, having mutually the deviation of orientation within about one degree, *e.g.* in Fig. 6 (99.8 % in purity, 18 cm./hr. in cooling velocity), indicating the result of the back reflection, each Laue spot is broken in a few spots. Therefore both the surface and the section structures of the single crystals prepared with three kinds of tin of 99.98, 99.8 and 98 percent in purity, were examined with microscope, after etching them with 50 percent nitric acid for a long time. Some of the results are given in Figs. 8~15: the so-called line structure is observed on the surface or the sectional plane parallel to the direction of the rod axis, (Figs. 8, 9, 11, 12, 14, 15), while on the sectional plane perpendicular to the direction of the axis, the cellular structures of various shapes are seen (Figs. 10, 13) and the same double cellular structure as those reported by G.D.Bengough[5], M.Smialowski[6] and M.J.Buerger[7] is occasionally detected (Fig. 13). Some of these line structures show the discontinuous lines (Fig.15).

It seemed that these line structures were already observed from the portion at which the single crystal began to from.

The width of the line structure was about 0.1 ~ 0.5 mm. and it was observed that the smaller the cooling velocity the larger the width became, *e.g.* as for the specimen lowered first at the cooling velocity of 12cm./hr., and then at 18 cm./hr., the width of the line structure in the part of 18 cm./hr. was smaller than that of the part of 12cm./hr. (Figs. 17,18,19).

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*In this study, the cooling velocity over 20 cm./hr. is up to 28 cm./hr.

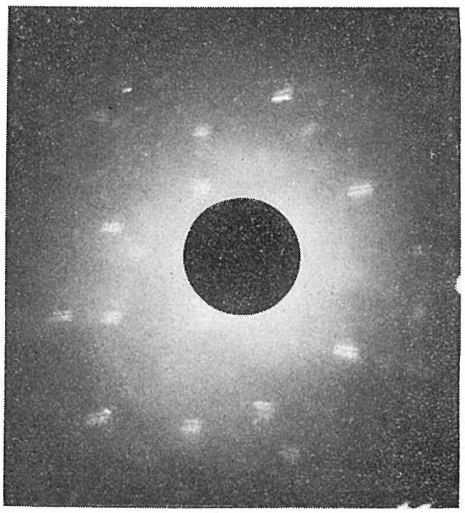

Fig. 5. 98%, 12cm./hr.

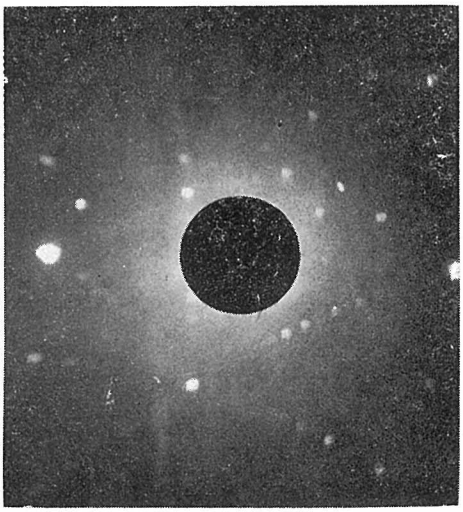

Fig. 6. 98%, 18cm./hr.

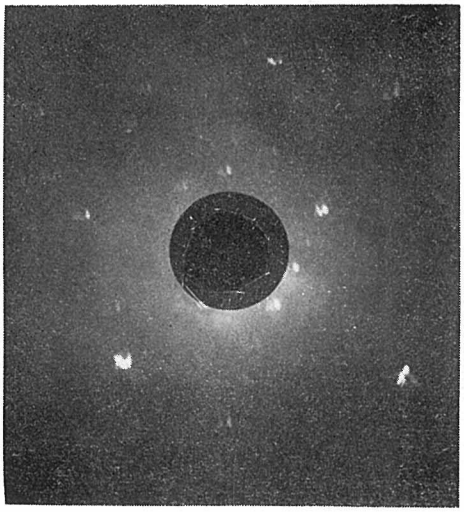

Fig. 7. 99.98%, 18cm./hr.

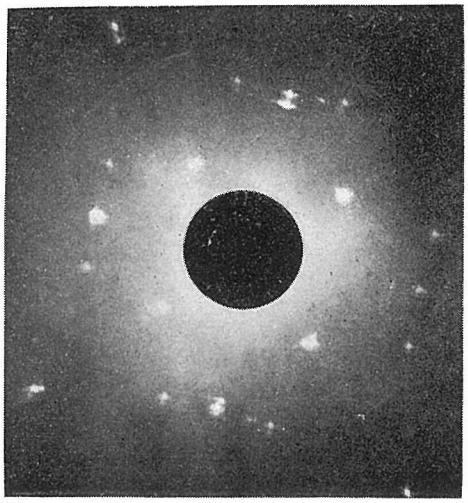

Fig. 20. 98%, 0.8cm./hr.

Back reflection Laue patterns

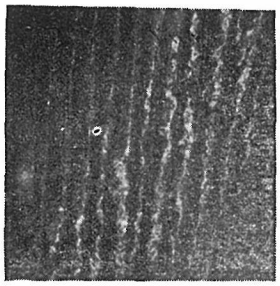

Fig. 8. 99.98%, 18cm./hr. ×20

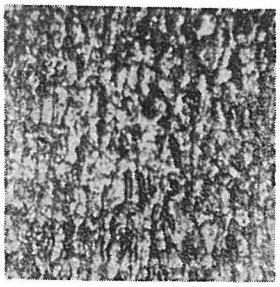

Fig. 9. 99.98%, 10cm./hr. ×20

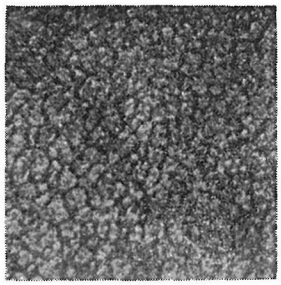

Fig. 10. 99.98%, 10cm./hr. ×20

Fig. 11. 99.8%, 20cm./hr. ×20

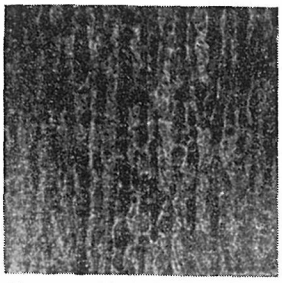

Fig. 12. 99.8%, 9cm./hr. ×20

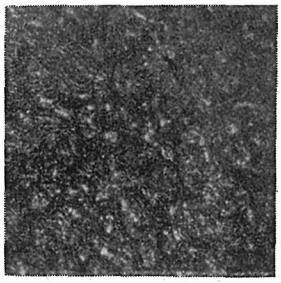

Fig. 13. 99.8%, 20cm./hr. ×20

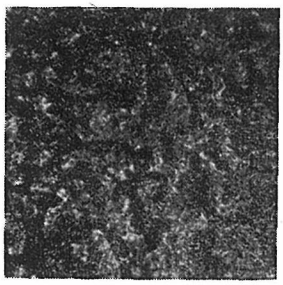

Fig. 14. 98%, 19cm./hr. ×20

Fig. 15. 98%, 12cm./hr. ×20

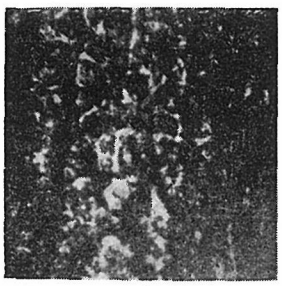

Fig. 16. 98%, 12cm./hr. ×20

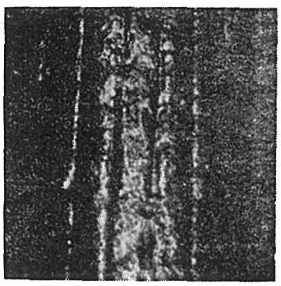

Fig. 17. 99.98%, 1.2cm./hr. ×20

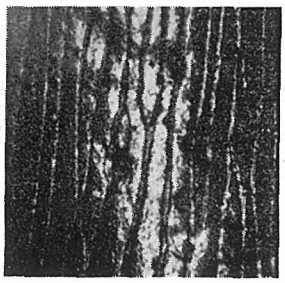

Fig. 18. 99.98% ×20

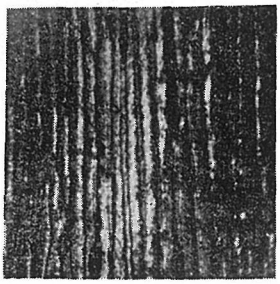

Fig. 19. 99.98%, 18cm./hr. ×20

Figs. 8,11,14 : Surface structure.
Figs. 9,12,15 : Longitudinal structure.
Figs. 10,13,16 : Transversal structure.
Fig. 16 : Thermal etched structure.
Fig. 18 : Intermediate structure.

On the other hand, it seemed that the lower the purity of the specimen, the wider the width of the line structure became in the case of the macro-observation (Figs. 8, 11, 14), but according to the back reflection X-ray analysis, the higher the purit yof the specimen, the fewer the rent of the Laue spots became (Figs. 5,6,7).

The same structure was observed when other specimen, which had not been etched, were thermal-etched at 220°C in vacuum of 10^{-3} mm. Hg. (e.g. Fig. 16). In this case, the structure was easily observed on the specimen of a low purity but hardly on that of a high purity.

No change of the line structure was detected after annealing the specimen having the line structure at 200°C for 20 hrs. in vacuum.

The glass mould holding tin was lowered, after holding it deliberately at the inclination of 30 degrees to the direction of the thermal gradient, but it was found that the direction of the line structure was not always parallel to the thermal gradient.

Under the consideration that the direction of line structures might be parallel to a certain crystal direction, the transmission Laue method was performed on the two specimens cut off perpendicularly to the line structure, and it resulted that the line structure was nearly parallel to the [110] direction.*

CONCLUSIONS

The results obtained in the present investigation can be summarized as follows :

(1) In the case of preparing tin single crystals by the mould type d shown in Fig. 1, the efficiency is almost 100 percent in the range of the cooling velocities up to 20 cm./hr.

(2) The direction of the rod axis of single crystals thus prepared is inclined at 75~90 degrees to the [001] direction in the range of cooling velocities of 4.5 ~ 11.0 cm./hr., but whether this direction is nearer to the [110] direction or [100] direction, can not be concluded.

(3) The single crystals prepared in this investigation are not ideal but the so-called line structures are observed, and the lower the purity of specimens the wider the width of these line structures becomes macroscopically, but it seems from the result of the back reflection X-ray analysis, that the higher the purity the fewer the rent of the Laue spots becomes. On the other hand, the larger the cooling velocity the larger the number of line structures becomes.

(4) The direction of the line structure is parallel to the [110] direction.

In conclusion, the writers wish to express their best thanks to Mr. Toshio Tanaka of

*The same investigation is now being performed with respect to the case of various low cooling velocities. In that case, the back reflection Laue pattern of the rod crystal (99.8 % in purity) produced under the condition of the cooling velocity of 0.8 cm./hr., is given in Fig. 20, clearly indicating that the direction of the line structure is parallel to the [110] direction.

the Mitsubishi Metals and Mining Co., who supplied them with some of the tin used in this experiment.

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